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Reaction of Germanium Tetrachloride with Chloro(phenyl)silanes in the Presence of Aluminum Chloride

V. I. Zhun', I. V. Sbitneva, and E. A. Chernyshev

State Research Institute of Chemistry and Technology of Organoelement Compounds, Russian State Research Center, Moscow, Russia

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Abstract—The effect of the quantity of aluminum chloride on the direction and depth of reaction of germanium tetrachloride with chloro(phenyl)silanes of the general formula Ph_nSiCl_{4-n} (n = 1–3) was studied to show that radical exchange between germanium and silicon is initiated only if the mixture contains no less than 2.5–5 wt% of aluminum chloride. With trichloro(phenyl)silane, the radical exchange is initiated at 5 wt% of aluminum chloride and results in exclusive formation of trichloro(phenyl)germane. The reactions of $GeCl_4$ with dichlorodiphenylsilane and chlorotriphenylsilane in the presence of 2.5–7.5 wt% of aluminum chloride give dichlorodiphenylgermane as the major product, and at $AlCl_3$ concentrations of above 10 wt% the major product becomes to be trichloro(phenyl)germane.

We previously observed exchange of phenyl radicals for chlorine in a mixture of dichloro(methyl)(phenyl)silane and germanium chloride, heated in the presence of 30–40 wt% of aluminum chloride [1]. More recently this reaction was studied in detail on an example of chloro(methyl)(phenyl)silanes [2, 3], but, like in [1], it was performed in the presence of 30–40 wt% of aluminum chloride. Proceeding with this research, we studied in the present work the effect of the quantity of aluminum chloride on the direction and depth of reaction of germanium tetrachloride with chloro(phenyl)silanes Ph_nSiCl_{4-n} (n = 1–3), as well as the possibility of radical exchange not only in the presence aluminum chloride, but also in the presence of other metal halides possessing Lewis acid properties (Table 1).

It was found that no reaction occurred in the presence of antimony trichloride, tin tetrachloride, or titanium tetrachloride, whereas the reaction with chloro(phenyl)silanes in the presence of boron trifluoride etherate gave fluoro(phenyl)silanes.

At the same time, chlorine at germanium in $GeCl_4$ exchanged for phenyl at silicon as the concentration of $AlCl_3$ was decreased to 5 wt% in the reaction with trichloro(phenyl)silane and to 2.5 wt% in the reactions with dichloro(phenyl)- and chlorotriphenylsilanes. The reaction with trichloro(phenyl)silane resulted in exclusive formation of trichloro(phenyl)germane.

$$PhSiCl_3 + GeCl_4 \xrightarrow{5\%\ AlCl_3} PhGeCl_3 + SiCl_4.$$

The reactions of $GeCl_4$ with dichlorodiphenylsilane and chlorotriphenylsilane in the presence of 2.5–7.5 wt% of aluminum chloride afforded dichlorodiphenylgermane as the major product, while at $AlCl_3$ concentrations of above 10 wt% the major product became to be trichloro(phenyl)germane.

$$Ph_nSiCl_{4-n} + GeCl_4 \xrightarrow{2.5\text{–}7.5\%\ AlCl_3} Ph_nSiCl_{5-n} + Ph_2GeCl_2,$$

$$Ph_nSiCl_{4-n} + GeCl_4 \xrightarrow{10\text{–}30\%\ AlCl_3} Ph_{n-1}SiCl_{5-n} + PhGeCl_3.$$

Obviously, as the fraction of aluminum chloride in the reaction mixture is increased, dichloro(diphenyl)-

Table 1. Reaction of Ph_2SiCl_2 with $GeCl_4$ (1:1) in the presence of various metal halides

Catalyst (%)	T, °C	Composition of the reaction mixture, %			
		$PhSiCl_3$	Ph_2SiCl_2	Ph_2SiF_2	$GeCl_4$
$SbCl_3$ (30)	100–110	4.1	51.2	–	44.6
$SbCl_3$ (50)	125–135	14.7	46.6	–	38.7
$BF_3 \cdot Et_2O$ (50)	125–135	–	–	15.0	38.7
$TiCl_4$ (50)	135	No reaction			

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Table 2. Reaction of Ph_nSiCl_n with $GeCl_4$ in the presence of $AlCl_3$

Ph_nSiCl_{4-n}	$Ph_nSiCl_{4-n}:GeCl_4$ ratio	Catalyst (%)	T, °C	Composition of the reaction mixture, %						
				$PhSiCl_3$	Ph_2SiCl_2	Ph_3SiCl	$PhGeCl_3$	Ph_2GeCl_2	$GeCl_4$	$SiCl_4$
$PhSiCl_3$	1:1	$AlCl_3$ (2.5)	115–125	No reaction						
$PhSiCl_3$	1:1	$AlCl_3$ (5)	115–125	45.2	–	–	2.8	–	46.3	5.7
$PhSiCl_3$	1:1	$AlCl_3$ (7.5)	115–125	39.8	–	–	4.9	–	44.9	10.4
$PhSiCl_3$	1:1	$AlCl_3$ (10)	115–125	40.4	–	–	46.1	–	8.9	4.5
$PhSiCl_3$	1:1	$AlCl_3$ (20)	115–125	16.9	–	–	49.8	–	27.9	5.4
$PhSiCl_3$	2:1	$AlCl_3$ (10)	145	49.3	–	–	38.3	–	7.5	4.9
$PhSiCl_3$	2:1	$AlCl_3$ (15)	150	47.1	–	–	36.5	–	10.9	3.5
$PhSiCl_3$	2:1	$AlCl_3$ (20)	155	36.1	–	–	28.5	–	32.6	2.9
Ph_2SiCl_2	1:1	$AlCl_3$ (2.5)	150	54.0	1.0	–	9.0	16.0	0.2	19.7
Ph_2SiCl_2	2:1	$AlCl_3$ (2.5)	130–135	44.3	19.3	–	0.2	22.5	13.7	–
Ph_2SiCl_2	1:1	$AlCl_3$ (3.5)	150	51.8	0.1	–	25.5	2.8	0.9	18.1
Ph_2SiCl_2	1:1	$AlCl_3$ (5)	135–145	29.9	1.1	–	40.4	4.7	16.7	6.3
Ph_2GeCl_2	1.35:1	$AlCl_3$ (5)	70–80	–	–	–	23.2	20.1	55.8	–
Ph_2SiCl_2	2:1	$AlCl_3$ (5)	110	58.9	1.8	–	4.8	27.6	–	6.3
Ph_2SiCl_2	1:1	$AlCl_3$ (10)	120–150	41.7	0.5	–	43.2	2.8	0.8	10.9
Ph_2GeCl_2	1.35:1	$AlCl_3$ (10)	100	–	–	–	73.4	–	–	–
Ph_2SiCl_2	1:1	$AlCl_3$ (20)	110	17.3	0.3	–	49.1	–	27.9	5.5
Ph_3SiCl	1:1	$AlCl_3$ (2.5)	150	No reaction						
Ph_3SiCl	1:1	$AlCl_3$ (5)	145	–	5.4	80.1	–	–	14.5	–
Ph_3SiCl	1:1	$AlCl_3$ (5)	150–155	1.6	35.5	49.3	–	0.8	12.8	–
Ph_3SiCl	1:1	$AlCl_3$ (7.5)	140	26.7	25.4	2.0	–	37.6	3.8	2.8
Ph_3SiCl	Excess $GeCl_4$ (1:1.5)	$AlCl_3$ (7.5)	145	37.9	–	–	11.5	46.4	1.0	2.1
Ph_3SiCl	1:1	$AlCl_3$ (10)	135	53.8	–	1.2	17.6	26.6	0.8	–
Ph_3SiCl	2:1	$AlCl_3$ (10)	135	13.5	54.9	7.5	–	18.2	4.8	–
Ph_3SiCl	3:1	$AlCl_3$ (10)	150–155	15.5	53.9	13.8	–	14.9	–	–
Ph_3SiCl	1:1	$AlCl_3$ (20)	125	67.3	–	–	28.7	0.5	–	–
Ph_3SiCl	1:1	$AlCl_3$ (30)	135	52.6	–	–	40.0	1.9	4.7	0.7
Ph_3SiCl	No $GeCl_4$ added	$AlCl_3$ (7.5)	140–145	–	29.8	70.2	–	–	–	–
Ph_3SiCl[a]	With $GeCl_4$ added (1:1)	$AlCl_3$ (7.5)	140	39.2	–	0.3	8.6	47.1	2.4	0.9

[a] $GeCl_4$ was added to preliminarily heated mixture of Ph_3SiCl with $AlCl_3$.

germane enter reaction with unreacred germanium tetrachloride to form trichloro(phenyl)germane. Evidence for this suggestion was obtained in a special experiment (Table 2).

$$Ph_2GeCl_2 + GeCl_4 \xrightarrow{10\%\ AlCl_3} 2PhGeCl_3.$$

EXPERIMENTAL

All experiments were performed with commercial reagents.

Reaction products were analyzed by GLC on an LKhM-80 chromatograph: metallic column 1000.3 mm, packing 5% SE-30 on Chromasorb G-AW-DMCS (0.15–0.18 mm); the oven temperature was programmed from 50 to 290°C at a rate of 12 deg min^{-1}. Injector temperature 320°C, thermal conductivity detector, detector temperature 300°C, detector current 90 mA. Carrier gas helium, rate 30 ml min^{-1}.

Reaction of chloro(phenyl)silanes with tetrachlorogermane. A mixture of chloro(phenyl)silane, tetrachlorogermane, and aluminum chloride was heated at 100°C for 3 h and then cooled and analyzed by GLC. The calculated product yields are given in Tables 1 and 2.

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